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U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

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**CONTROL OF MASS TRANSPORT  
OF DISSEMINATED LIQUIDS AND VAPORS:  
CROSS-LINKED POLYMERIC PARTICLE SURVEY AND  
SORPTION EXPERIMENTATION**

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Wendel J. Shuely

RESEARCH AND TECHNOLOGY DIRECTORATE

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Aberdeen Proving Ground, MD 21010-5423

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## PREFACE

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1. INTRODUCTION

1.1 Classification of Mass Transport Control Mechanisms.

A general mass transport process exists that consists of transfer of a bulk mass of fluid to a fluid dispersed over a predefined surface area. The scale of this process can range from small enclosed, industrial processes to large dispersals over large areas of the environment.<sup>1</sup> Strategies and mechanisms for control of this mass transport process can be divided into those mechanisms that employ additives to alter the fluid properties or geometry and those that employ the unaltered fluid. The additives employed can be further divided into the following two classes:

- Monolithic additives control the structure and/or geometry of the fluid at the smallest geometrical unit of mass transport (e.g., particles and other carrier structures).

- Continuum additives alter the fluid properties (i.e., viscoelasticity and surface tension) that control mass transport but do not impose a prestructured particle size or geometry on the fluid.

Given these classifications of fluid mass transport mechanisms, one can define the scope of this review and investigation as limited to that of control by monolithic additives. A brief survey of the advantages and limitations of each class will be given. A further classification of monolithic additives will be provided based on composition (e.g., cross-linked polymers, porous inorganic particles), geometry (spherical, disk, rod), and mechanical properties (deformable, brittle).

1.2 Review.

Several general references on mass transport control are listed in the bibliography section. Also listed in the bibliography are more specific publications involving research in our laboratories with cross-linked polymer particles, often called imbiber beads (Dow Chem, Midland, MI) or sorptive particles.

The chemicals that had approvals for chamber and environmental testing were reviewed. Those chemicals with existing data sets on dissemination control with continuum additives were identified for comparative experimentation with monolithic cross-linked polymer additives. The test chemicals identified were triethylphosphate (TEPO), tributylphosphate (TBPO), and dibutylphthalate (DBP).

## 2. EXPERIMENTATION

### 2.1 Materials.

#### ● Polymeric Materials.

Previous research on particles was reviewed and an inventory of selected cross-linked particles is provided in Table 1. The first column identifies the polymer composition, identification, and lot number; and the second column lists available information on particle size. The next column provides general remarks on source or preparation; the quantity of limited experimental samples is also provided.

### 2.2 Chemicals.

The chemicals employed as environmentally and/or safety approved dissemination test fluids and sorbates for the polymeric materials are listed in Table 2. The chemical name, code, and source are listed in the sequential columns.

### 2.3 Procedures.

The predictive methods were based on polymer phase diagram theory.<sup>2,3</sup> The experimental procedure followed ASTM D3132.<sup>4</sup>

## 3. RESULTS

#### ● Polymer-Liquid Interaction Screening Experiments.

One initial set of experiments in mass transport studies involves selecting polymer-liquid pairs for study employing theoretical phase diagram calculations and confirmatory experiments.<sup>5</sup> A set of sorption screening experiment results are recorded in Table 3. The codes for the polymer-liquid pair are listed in the first column and sorption results are noted in adjacent column(s). All candidate polymer-liquid pairs resulted in soluble/sorbed systems, confirming the phase diagram predictions.

## 4. DISCUSSION AND CONCLUSIONS

The formulation, rheology, and breakup of viscoelastic and particulate dissemination fluids have been extensively studied in our laboratory; however, a direct comparison at ultra-high stress rates has never been an issue. In preparation for ongoing studies comparing viscoelastic versus particulated dissemination mechanisms, distinction has been drawn between these two transport control mechanisms. The environmentally approved test liquids employed with viscoelastic additives in previous test programs were identified. Polymer phase diagrams were employed to predict and select candidate sorptive polymers. All predictions were successful and resulted in sorption into the cross-linked candidate polymers. Therefore, several candidate systems of sorbed particles in test liquids are now available for comparative dissemination testing and mass transport experimentation.

Table 1. Cross-Linked Polymeric Particles Employed  
to Control Fluid Mass Transport

Polymer Particle Composition/Lot	Code	Size	Remarks	Quantity Available
Dow Imbiber Bead TC Lot 08689-38	DIB-TC	>20 mesh		20 g
Dow Imbiber Bead T-32	DIB-T32			10 g
Dow Imbiber Beads - S No. S-0110.52	DIB-S	~500 m	1974	100 g
Dow Imbiber Bead T32 poly(t-butyl styrene)	DIB-T32	1 mm		50 g
Dow Imbiber Bead Lot N, FPS 400ZL-PTBS	DIB-FPS			
Dow Imbiber Bead T Lot XE-01-00-31	DIB-T	<200		20 g
Dow Imbiber Beads T	DIB-T 2mm	2 mm	Experimental Lot	
Dow Imbiber Beads T	DIB-TXE	>>3-5 mm		
Dow Imbiber Bead S	DIB-S			500 g
Dow Imbiber Bead TC	DIB-TC			400 g
Dow Imbiber Bead T	DIB-T			400 g
LU-Bust 3080-1	LU-BUST1		Lehigh U.	
LU-Bust 3080-2	LU-BUST2		Lehigh U.	
Poly(50% vinylacetate-co-50% m-vinyl pyrrolidine-co <1.0% DVB)	PVA-PVP	1/4 Rods	Lehigh U. 1984	200 g
Poly(butylmethacrylate-co-.02 vol % DVB)	PIBM-Bulk	1" dia	LTC Kopchick Bulk polymerized	3 beads
Poly(methylmethacrylate)	PMMA	1"	LTC Kopchick Bulk polymerized	1 bead each
Poly(MMA-co-acrylate)	PMMA-Ac			
Poly(methylmethacrylate) Shock Hydrodynamic Run 8	PMA-SH	10 beads		
Poly(MMA-co-styrene) NAS Beads	PMMA-S	Small		500 g
Sustrelle Microbeads		<75 m	Aqueous	

Table 1. Cross-Linked Polymeric Particles Employed to Control Fluid Mass Transport (Continued)

Poly(styrene-co-0.02-DVB) P649002PN, Lot L900531A	PS-Bng	650 $\mu$	1000 $\mu$ max	1 kg
Polystyrene CT-Macrobead 1/4	PS-MB	5 mm	Not cross-linked	100 g
Polystyrene Cross-Linked Rods Goodfellow Corp.	PS-Rod	> 10 mm	Cut from rods	

Table 2. Chemicals Employed in Sorption Screening Experiments

Chemical	Code	Source
Triethyl phosphate	TEPO	Aldrich
Tributyl phosphate	TBPO	Ashland
Dibutyl Phthalate	DBP	Aldrich

Table 3. Sorption Screening Experimental Results for Polymer-Liquid Pairs: Tributylphosphate (TBPO) Example

Liquid Code	Polymer Code (see Table 1)	Predicted Interaction (S = Sorption)	Sorption Results
TBPO	DIB-TXE	S	S
TBPO	DIB-T 2 mm	S	S
TBPO	PS-Bng	S	S
TBPO	LU-BUST1	S	S
TBPO	LU-BUST2	S	S
TBPO	PS-Bng	S	S
TBPO	PIBM-Bulk	S	S
TBPO	PS-MB	S	S, dissolved

## LITERATURE CITED

1. Fan, Liang-Tseng, Controlled Release: A Quantitative Treatment, Springer-Verlag, Berlin, 1989.
2. Taft, Robert W.; Shuely, Wendel J.; Doherty, Ruth M.; and Kamlet, Mortimer J.; "Linear Solvation Energy Relationships. 39. A Multiple Substituent Parameter Equation for  $\rho$  Values (Hydrogen Bond Acceptor Basicities) of  $XYZP=O$  Compounds," J. Org. Chem. Vol. 53, pp 1737-1741 (1988).
3. Shuely, Wendel J., "Integration of Test Methodology, Material Database, and Material Selection/Deselection Strategies for a Chemical-Material Compatibility System," In Proceedings of the Fourth International Symposium on the Computerization and Use of Materials Property Data, NIST/ASTM, Gaithersburg, MD, October 1993.
4. Solubility Range of Resins and Polymers, ASTM D3132, ASTM, Philadelphia, PA, 1989.
5. Shuely, Wendel J., "Test Methodology for Development of Corrosion Resistant Polymeric Materials: Predictive and Experimental Methods for Chemical Resistance Screening," In Proceedings of the 12th Biennial Symposium on Managing Corrosion with Plastics, Volume XI, Chap. 19, pp 19-1 to 19-17, November 1993.

## BIBLIOGRAPHY

1. Vanderhoff, J.W., Earhart, K.A., and Kang, M.H.J., Synthesis, Sorption, and Desorption of Large Imbiber Beads, CRDC-CR-84029, U.S. Army Chemical Research and Development Center, Aberdeen Proving Ground, MD, June 1984, UNCLASSIFIED Report. (AD B086 233L)
2. Walker, Helen M., and Penski, Elwin C., Enhancement of the Persistency of N-Butyl Mercaptan with Imbiber Beads and PEG-200, ARCSL-TR-81042, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, September 1981, UNCLASSIFIED Report. (AD B060 323L)
3. Walker, Helen M., Szafraniec, Linda L., and Penski, Elwin C., EA 4923 Imbiber Bead Behavior, ARCSL-TR-79069, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, May 1981, UNCLASSIFIED Report. (AD B057 793L)
4. Penski, Elwin C., and Walker, Helen M., Droplet Evaporation Measurement Methods and the Evaporation of Neat EA 4923 and of EA 4923 from Imbiber Beads, EC-TR-76052, Edgewood Arsenal, Aberdeen Proving Ground, MD, August 1976, UNCLASSIFIED Report. (AD C007 333)
5. Das, K.G., Ed., Controlled Release Technology, Wiley Inc., New York, NY, 1983.
6. Rosoff, Morton, Ed., Controlled Release of Drugs: Polymers and Aggregate Systems, VCH Publishers, New York, NY, 1989.